Journal of Photochemistry and Photobiology A: Chemistry 106 (1997) 37–43

Effect of an external electric field on photoinduced interlayer electron transfer in Langmuir–Blodgett films as revealed by the effect of the field on fluorescence: a D–A system of thiacyanine and viologen

Nobuhiro Ohta *, Tatsuya Nomura, Iwao Yamazaki

Department of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060, Japan

Abstract

Electron donor and acceptor layers separated by a spacer layer were prepared with thiacyanine and viologen using the Langmuir–Blodgett technique, and the effect of an external electric field on the fluorescence of thiacyanine was examined. Interlayer electron transfer from the photoexcited molecules of thiacyanine to viologen was affected by the external electric field. The magnitude and direction of the field-induced change in the electron transfer rate were evaluated on the basis of measurements of the field-induced change in the fluorescence intensity combined with fluorescence decay measurements. © 1997 Elsevier Science S.A.

Keywords: External electric field; Langmuir–Blodgett films; Photoinduced interlayer electron transfer; Thiacyanine; Viologen

1. Introduction

A radical–ion pair produced by an electron transfer process usually has a large dipole moment, and the energy gap between the reactant and the product (radical–ion pair) is expected to be shifted significantly by an electric field. Thus the electron transfer rate may be affected by an electric field since it is dependent on the energy gap between the reactant and product states of the electron transfer process [1,2]. The energy shift depends not only on the magnitude of the electric dipole moment of the radical–ion pair, but also on the orientation of the dipole moment relative to the direction of the applied field. Studies on the effect of an electric field on photoinduced electron transfer processes are important in order to obtain a thorough understanding of the mechanism of these processes, including transfer in biological systems [3]. These studies are also important for the control of chemical processes related to photoinduced electron transfer and also for the design of molecular devices, such as molecular photodiodes [4].

When electron donor and acceptor molecules are distributed in a homogeneous system, e.g. in solution or in an organic polymer film, there exists a distribution of donor–acceptor distances with a random orientation. When an external electric field is applied in a homogeneous system, different pairs of donors and acceptors show different magnitudes of field effect, and the analysis of the effect is very complicated. The Langmuir–Blodgett (LB) technique is an excellent method for the preparation of an ultrathin film with a well-defined molecular order. Using LB films, molecular assemblies which show photoinduced electron transfer in a definite direction can be easily prepared. Therefore an LB film is one of the best objects for the investigation of the effect of an electric field on electron transfer processes since the molecular orientation and arrangement with respect to the direction of the externally applied electric field can be well defined.

When monolayers of cyanine dye and amphiphilic viologen are deposited with a spacer layer, interlayer electron transfer processes from photoexcited cyanine dye to viologen occur on the basis of excited donor steady state fluorescence quenching experiments [5–7]. The most remarkable result is the extraordinarily long range of photoinduced electron transfer which can be observed even for a spacing of nearly 3 nm. Such a long-range electron transfer produces a radical–ion pair whose electric dipole moment is extremely large, and a large electric field effect may be expected on the rate of such a long-range electron transfer process.

In this study, the effect of an external electric field on the rate of interlayer electron transfer between photoexcited thiacyanine and viologen, separated by a fatty acid monolayer of well-defined thickness, was examined on the basis of meas-

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* Corresponding author. Tel.: +81 11 706 6607; fax: +81 11 709 2037; e-mail: nohta@eng.hokudai.ac.jp

PII S1010-6030(97)00036-1

urements of the field-induced change in the steady state fluorescence intensity combined with fluorescence decay measurements of thiacyanine. Even in the absence of viologen, the fluorescence of thiacyanine doped in LB films is affected by an external electric field, as mentioned previously [8]. The effect of the field on the rate of electron transfer between photoexcited thiacyanine and viologen was examined by comparing the effect of the field on the fluorescence of thiacyanine in the absence and presence of viologen.

2. Experimental details

N,N′-Dioctadecylthiacyanine perchlorate (Nippon Kanko Shinkiso), hereafter denoted by TC, was used without further purification. *N,N′*-Dioctadecyl-4,4′-bipyridinium dibromide, hereafter denoted by VIO, was synthesized according to Ref. [9]. Commercially available arachidic acid (AA), stearic acid (SA) and methyl arachidate (MA) were purified by recrystallization from acetone. All samples of the LB films were deposited as cadmium salts.

A mixture of AA and MA (ratio, 1 : 1), denoted by AA–MA, was used as a matrix. Two different mixing ratios between TC and AA–MA, i.e. 10 and 20 mol.%, were employed. In the mixture of VIO and AA–MA, the concentration of VIO was 10 mol.%. In this study, two kinds of stacked multilayer film were prepared: one included a VIO film (sample I) and the other did not (sample II). Sample II was prepared as follows. Initially, seven layers of AA were pre-coated on the quartz substrate. This was followed by the deposition of two monolayers composed of TC and AA–MA with a spacer composed of one layer of SA and five layers of AA between the adjacent mixed layers. Finally, one layer of SA and seven layers of AA were post-coated. These stacked multilayer films were of Y type, except for the AA film deposited following the SA film, and the hydrophilic group of TC contacts with the hydrophilic group of SA. In these films, all TC molecules have the same orientation with respect to the electrode. In sample I, only the monolayer film of AA deposited following the SA film was replaced by a VIO mixed film. It should be noted that SA was deposited as a spacer in sample I between the TC monolayer film and the VIO film. A schematic illustration of the TC, SA and VIO films in sample I is shown in Fig. 1. The LB films deposited on one side of the substrate were wiped off and only the LB films deposited on the other side were used for the optical measurements in each case. The monolayer film composed of a mixture of TC and AA–MA and the film of AA or SA were deposited at 25 mN m^{-1}. The thickness of each layer was 25 Å for SA and 27.3 Å for AA and AA–MA [10], yielding a total thickness of the LB film of 623.3 Å. The applied field strengths were calibrated by dividing the applied voltage by these thicknesses.

A transparent aluminium film evaporated on a quartz plate was used as an electrode. Following the deposition of the above-mentioned multilayer films on the aluminium-coated plate, a transparent aluminium film was again coated, as another electrode, by evaporation. External electric fields were applied up to 1.5×10^6 V cm^{-1}.

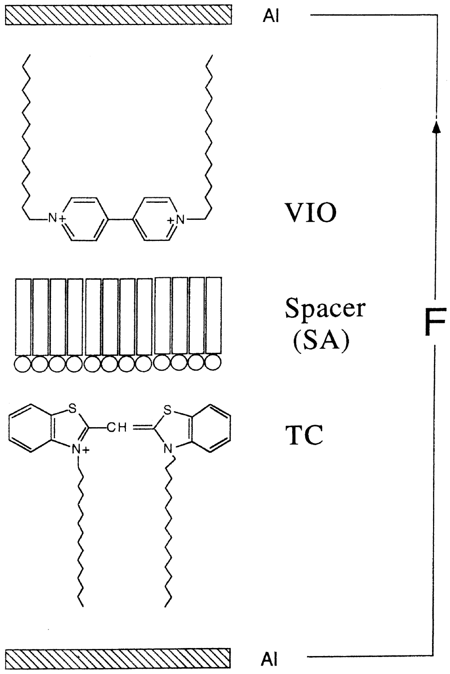

Fig. 1. Schematic illustration of LB multilayer films of TC and VIO separated with a spacer of SA.

All the fluorescence measurements were carried out at room temperature with a spectrometer equipped with an electric field modulation apparatus. Light from a 150 W xenon lamp dispersed by a monochromator was focused on the sample in vacuo. Fluorescence emitted at a right angle to the excitation light was dispersed by a monochromator and detected by a photomultiplier. A sinusoidal a.c. voltage was applied between the electrodes of the sample using a function generator (Iwatsu FG 350). For the measurement of the field-induced fluorescence modulation spectra, i.e. electrofluorescence spectra, a small amount of the a.c. component of the fluorescence intensity at wavelength λ ($\Delta I_F(\lambda)$), synchronized with the applied voltage, was detected with a lock-in amplifier (NF, LI-574 and P-51) at the first harmonic (1f) and second harmonic (2f) of the modulation frequency (typically 20 Hz) as a function of λ, together with the total fluorescence intensity, at a fixed excitation wavelength. For the measurement of the field-induced excitation spectra, an a.c. component of the fluorescence intensity was detected as a function of the excitation wavelength by fixing the wavelength of monitoring fluorescence.

The electric-field-induced change in the absorption intensity, i.e. the so-called electroabsorption spectrum, was also measured at room temperature at atmospheric pressure using the method described previously [11].

Fluorescence decays were measured using a mode-locked titanium–sapphire laser (Coherent, Mira 900) pumped by an argon ion laser (Coherent, Innova 300) combined with a pulse picker (Coherent, model 9200). An excitation wavelength of 390 nm was employed and detection was performed with a single-photon counting system [12].

3. Results and discussion

The steady state fluorescence of TC in sample I is weaker than that in sample II at both 10 and 20 mol.% of TC, indicating that TC fluorescence is quenched by VIO. The quenching of TC fluorescence is also confirmed by measurements of the time-resolved intensity ($(I_f(t))$) of TC fluorescence, as shown in Fig. 2. Here, t represents the time. The fluorescence decay rate is faster in the presence of VIO. Thus there is no doubt that the fluorescence of TC is quenched by VIO probably as a result of interlayer electron transfer from photoexcited TC to VIO in LB films, as suggested by Kuhn [5,7] and Möbius [6]. The fluorescence shows a non-exponential decay in LB films (see Fig. 2), and these decays can be analysed by a multiexponential function. At 10 mol.% of TC in the absence of VIO, for example, the fluorescence decay is reproduced by assuming a triple exponential function, where the lifetimes of the components are estimated to be 0.35, 1.23 and 2.83 ns. In the present treatment, the average lifetime, denoted by τ_F, was determined by calculating $\int I_f(t)\mathrm{d}t/I_f(0)$ (the average lifetime was estimated with $\int tI_f(t)\mathrm{d}t/\int I_f(t)\mathrm{d}t$ in Ref. [8], but the present definition seems to be more plausible as the average value). The τ_F values at 10 and 20 mol.% of TC were determined to be 0.94 and 0.71 ns respectively in the absence of VIO and 0.64 and 0.50 ns respectively in the presence of VIO. By assuming that the change in τ_F is induced by electron transfer from photoexcited TC to VIO, the average rate constants of electron transfer, denoted by k_{et}, are determined to be 5.0×10^8 s^{-1} and 7.0×10^8 s^{-1} at 10 and 20 mol.% of TC respectively.

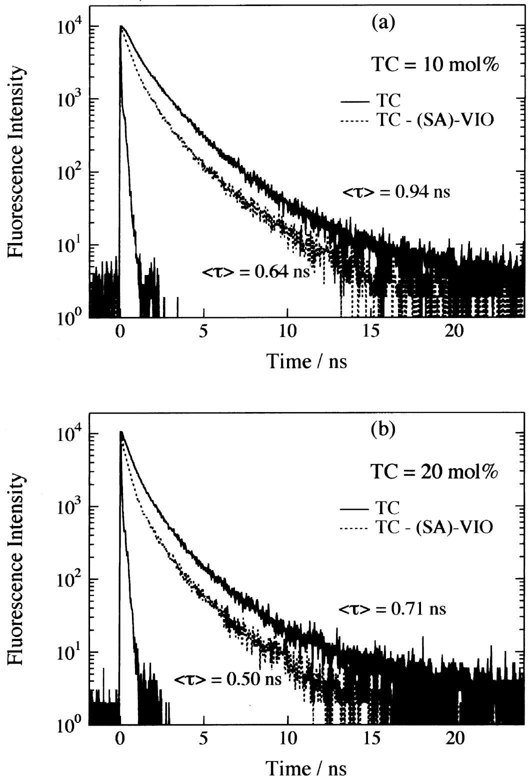

Fig. 2. Fluorescence decays of TC at 10 mol.% (a) and 20 mol.% (b). Full and dotted lines show the decays for the samples without and with VIO (10 mol.%) respectively. The excitation pulse shape is also shownin the figure. Excitation and monitoring wavelengths were 410 and 500 nm respectively. The average lifetime is shown in the figure.

When an electric field is applied with the direction given in Fig. 1, fluorescence quenching is induced both as a linear (1f) and quadratic (2f) field effect in the absence of VIO, as mentioned previously [8]. The 1f electrofluorescence spectra of TC observed at 20 mol.% of TC in the absence of VIO are shown in Fig. 3(a′) and Fig. 3(b′), together with the fluorescence spectra. When the direction of $\boldsymbol{F}$ is inverted, the sign of $\Delta I_F(\lambda)$ at 1f is changed, indicating that the fluorescence enhancement is induced as a linear effect with the direction of $\boldsymbol{F}$ opposite to that given in Fig. 1. It should be noted that the 2f electrofluorescence spectra are independent of the direction of $\boldsymbol{F}$, and only fluorescence quenching is induced as a quadratic effect. The shapes of the 1f and 2f electrofluorescence spectra are very similar to those of the fluorescence spectra at both 10 and 20 mol.% of TC, suggesting that the effect of the field on the fluorescence intensity is dominated by a change in the fluorescence quantum yield.

Similar electrofluorescence spectra were observed in the presence of VIO at both 1f and 2f (see Fig. 3(a) and Fig. 3(b) for the 1f spectra at 20 mol.% of TC). However, the magnitude of ΔI_F in the presence of VIO is smaller than that in the absence of VIO (cf. Fig. 3(a) and Fig. 3(a′)). Plots of $\Delta I_F(\lambda)/I_F(\lambda)$ as a function of the strength of the applied electric field ($\boldsymbol{F}$) were obtained at $\lambda = 480$ nm at both 1f and 2f. The results for 20 mol.% of TC are shown in Fig. 4. Plots of $\Delta I_F/I_F$ similarly observed for 10 mol.% of TC at 1f are shown in Fig. 5. It should be noted that the results shown in Fig. 4 and Fig. 5 were obtained with the field direction shown in Fig. 1. When the direction of $\boldsymbol{F}$ is inverted, the magnitude of the slope of $\Delta I_F/I_F$ remains essentially the same, but the sign of the slope at 1f is changed in both the absence and presence of VIO. However, the 2f spectra are independent of the field direction, as mentioned above.

Strictly speaking, the 1f spectrum in the presence of VIO at 10 mol.% of TC is different from the fluorescence spectrum, especially in the shorter wavelength region, and the peak of the 1f spectrum shows a slight red shift, as observed in Fig. 3(b). This result indicates that ΔI_F resulting from the first Stark shift, which shows a spectral distribution given by the first derivative of the fluorescence spectrum and can be ignored in the absence of VIO, is not negligible in the presence of VIO because the field-induced change in the fluorescence quantum yield is smaller. It should be noted that the plots shown in Fig. 4 and Fig. 5 were obtained by monitoring the fluorescence at the maximum of 480 nm, where ΔI_F given by the first Stark shift is considered to be negligible. It should also be noted that the results shown in Figs. 3–5 were obtained on excitation at 395 nm, where the field-induced

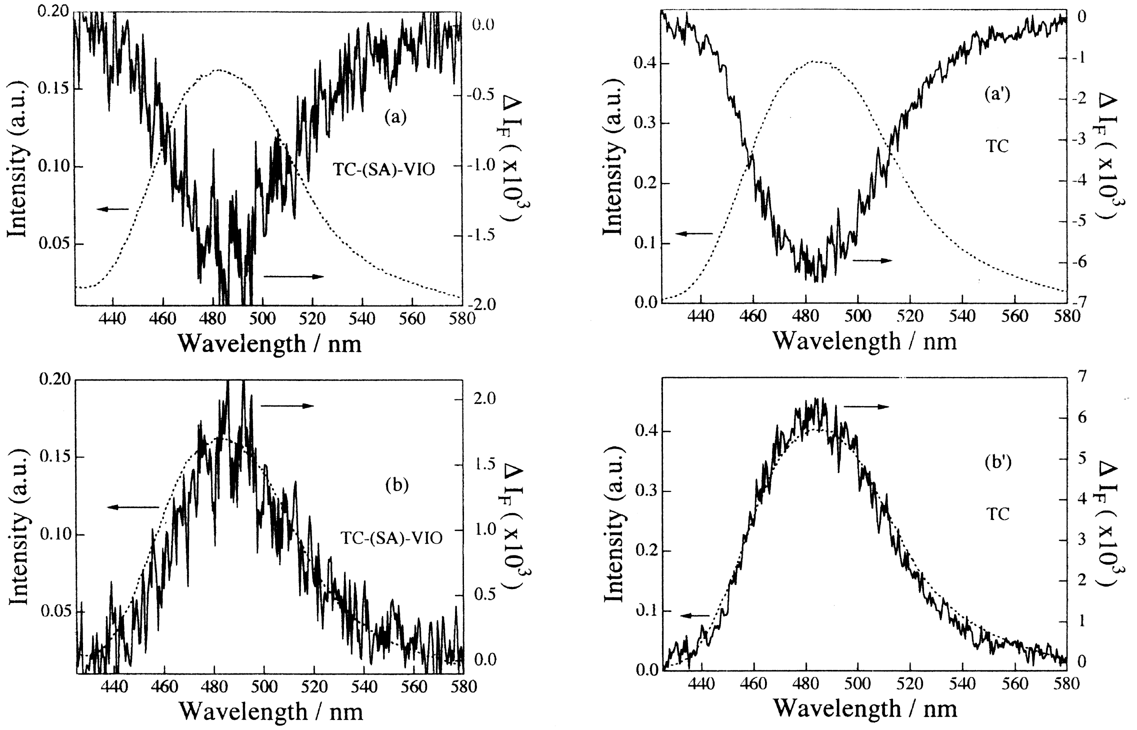

Fig. 3. Electrofluorescence spectra of TC (20 mol.%) in LB films (full line) with 10 mol.% of VIO (left: (a) and (b)) and without VIO (right: (a′) and (b′)) observed at 1f, together with the fluorescence spectrum (dotted line). The top two spectra were obtained with the field direction shown in Fig. 1, and the bottom two spectra were obtained with the opposite field direction. The applied field strength was 1.35×10^6 V cm^{-1} and the excitation wavelength was 395 nm.

change in the absorption intensity is negligibly small [8]. Thus the field-induced change in ΔI_F shown in Fig. 4 and Fig. 5 is considered to originate from a field-induced change in the fluorescence quantum yield.

As clearly shown in Fig. 4 and Fig. 5, the magnitude of $\Delta I_F/I_F$ of the TC fluorescence at 1f decreases on deposition of a VIO monolayer film, whereas $\Delta I_F/I_F$ at 2f in both the absence and presence of VIO remains almost constant. The fact that the field-induced change in the fluorescence quantum yield depends on the existence of VIO is also confirmed by the electrofluorescence excitation spectra. Fig. 6 shows the electrofluorescence excitation spectra of 10 mol.% of TC in the absence and presence of VIO, together with the fluorescence excitation spectra. These spectra were obtained at 1f by monitoring the fluorescence at 480 nm. The magnitude of $\Delta I_F/I_F$ is smaller in the presence of VIO than in its absence. Furthermore, the shape of the electrofluorescence excitation spectrum in the presence of VIO is very different from the fluorescence excitation spectrum and quite similar to the electroabsorption spectrum given previously [8]. These results show that the contribution of the field-induced change in the absorption intensity increases in the presence of VIO because the field-induced change in the fluorescence quantum yield decreases in the presence of VIO. The electrofluorescence excitation spectra observed in the absence of VIO do not agree with the fluorescence excitation spectra; $\Delta I_F/I_F$ at a peak in the longer wavelength region is smaller than that at a peak in the shorter wavelength region. This disagreement implies that different species of TC show different electric field effects on fluorescence. The effect of the field on the TC fluorescence of a dimer is considered to be more efficient than that on a monomer, as suggested previously [8].

The field-induced change in the quantum yield of TC fluorescence is proposed to be caused by the field-induced change in the electron transfer rate. Two different electron transfer processes are assumed to exist in the present TC–VIO system: one involves electron transfer between photoexcited TC and the cadmium salt of SA deposited as a spacer, and the other involves electron transfer from photoexcited TC to VIO.

The quantum yield of TC fluorescence at zero field and its field-induced change in the presence of VIO are denoted by Φ_F^{VIO} and $\Delta\Phi_F^{VIO}$ respectively. By assuming that the relaxation processes of the excited molecules are irreversible, Φ_F^{VIO} and $\Phi_F^{VIO}+\Delta\Phi_F^{VIO}$ are given by $k_r/(k_r+k_{nr}+k_{et}^{SA}+k_{et}^{VIO})$ and $k_r/(k_r+k_{nr}+k_{et}^{SA}+\Delta k_{et}^{SA}+k_{et}^{VIO}+\Delta k_{et}^{VIO})$ respectively. Here, k_r and k_{nr} represent the rate constants of the radiative and non-radiative processes other than electron transfer respectively. k_{et}^{SA} and Δk_{et}^{SA} are the electron transfer rate between TC and SA at zero field and its field-induced change respectively. k_{et}^{VIO} and Δk_{et}^{VIO} are the rate of electron transfer from photoexcited TC to VIO and its field-induced change respectively. The average fluorescence lifetimes in the absence and presence of VIO, which are denoted by τ_F and τ_F(VIO) respectively, are assumed to be given by $1/(k_r+k_{nr}+k_{et}^{SA})$ and $1/(k_r+k_{nr}+k_{et}^{SA}+k_{et}^{VIO})$. Thus Δk_{et}^{SA}

and $\Delta k_{\mathrm{et}}^{\mathrm{VIO}}$ are related to $\Delta \Phi_{\mathrm{F}}^{\mathrm{VIO}} / \Phi_{\mathrm{F}}^{\mathrm{VIO}}$ and $\tau_{\mathrm{F}}(\mathrm{VIO})$ by the following equation

$$\begin{aligned}\Delta k_{\mathrm{et}}^{\mathrm{SA}} + \Delta k_{\mathrm{et}}^{\mathrm{VIO}} &= [-\Delta \Phi_{\mathrm{F}}^{\mathrm{VIO}} / (\Phi_{\mathrm{F}}^{\mathrm{VIO}} \\ &\quad + \Delta \Phi_{\mathrm{F}}^{\mathrm{VIO}})] / \tau_{\mathrm{F}}(\mathrm{VIO}) \\ &= -(\Delta \Phi_{\mathrm{F}}^{\mathrm{VIO}} / \Phi_{\mathrm{F}}^{\mathrm{VIO}}) / [1 \\ &\quad + (\Delta \Phi_{\mathrm{F}}^{\mathrm{VIO}} / \Phi_{\mathrm{F}}^{\mathrm{VIO}})] / \tau_{\mathrm{F}}(\mathrm{VIO})\end{aligned} \qquad (1)$$

By using the average fluorescence lifetime, the quantum yield of TC fluorescence at zero field and its field-induced change in the absence of VIO, denoted by τ'_{F}, Φ'_{F} and $\Delta \Phi'_{\mathrm{F}}$ respectively, $\Delta k_{\mathrm{et}}^{\mathrm{SA}}$ is given by the following equation

$$\Delta k_{\mathrm{et}}^{\mathrm{SA}} = -(\Delta \Phi'_{\mathrm{F}} / \Phi'_{\mathrm{F}}) / [1 + (\Delta \Phi'_{\mathrm{F}} / \Phi'_{\mathrm{F}})] / \tau'_{\mathrm{F}} \qquad (2)$$

$\Delta k_{\mathrm{et}}^{\mathrm{SA}}$ was determined using Eq. (2) employing the values of $\Delta I_{\mathrm{F}}(\lambda)/I_{\mathrm{F}}(\lambda)$ and the average fluorescence lifetime observed at $\lambda = 500$ nm instead of $\Delta \Phi'_{\mathrm{F}}/\Phi'_{\mathrm{F}}$ and τ'_{F}. Similarly, $\Delta k_{\mathrm{et}}^{\mathrm{SA}} + \Delta k_{\mathrm{et}}^{\mathrm{VIO}}$ was determined using the average fluorescence lifetime and $\Delta I_{\mathrm{F}}/I_{\mathrm{F}}$ observed in the presence of VIO instead of $\tau_{\mathrm{F}}(\mathrm{VIO})$ and $\Delta \Phi_{\mathrm{F}}/\Phi_{\mathrm{F}}$. By combining these values with the above-mentioned value of $\Delta k_{\mathrm{et}}^{\mathrm{SA}}$, $\Delta k_{\mathrm{et}}^{\mathrm{VIO}}$ was determined. Hereafter, $\boldsymbol{F}$ is given in units of V cm^{-1}. The values of $\Delta k_{\mathrm{et}}^{\mathrm{SA}}$ and $\Delta k_{\mathrm{et}}^{\mathrm{VIO}}$ at 20 mol.% of TC are given as follows in units of s^{-1}

$$\Delta k_{\mathrm{et}}^{\mathrm{SA}}(\text{at 20 mol.\%}) = 1.8 \times 10\,\boldsymbol{F} + 1.5 \times 10^{-6}\,\boldsymbol{F}^2 \qquad (3a)$$

$$\Delta k_{\mathrm{et}}^{\mathrm{VIO}}(\text{at 20 mol.\%}) = -2.6\,\boldsymbol{F} + 6.2 \times 10^{-7}\,\boldsymbol{F}^2 \qquad (3b)$$

As far as the linear field dependence is concerned, $\Delta k_{\mathrm{et}}^{\mathrm{SA}}$ and $\Delta k_{\mathrm{et}}^{\mathrm{VIO}}$ at 10 mol.% were estimated to be $4.5\boldsymbol{F}$ and $-1.5\boldsymbol{F}$ in units of s^{-1} respectively. These results show that the rate constant of electron transfer from TC to VIO is reduced by $\boldsymbol{F}$ with the field direction given in Fig. 1, whereas electron transfer between TC and SA is enhanced by $\boldsymbol{F}$, irrespective of the concentration of TC. Furthermore, these equations show that the former process is enhanced, whereas the latter process is reduced, by $\boldsymbol{F}$ when a field in the opposite direction is applied.

According to Marcus theory [13,14], the rate constant of electron transfer is given by

$$k_{\mathrm{et}} = \frac{2\pi}{\hbar} \frac{J^2}{(4\pi k_{\mathrm{B}} T \lambda_0)^{1/2}} \exp\left[-\frac{(\Delta G + \lambda_0)^2}{4 k_{\mathrm{B}} T \lambda_0}\right] \qquad (4)$$

where J, $\hbar$, k_{B}, T and ΔG are the transfer integral, the Planck constant divided by 2π, the Boltzmann constant, the temperature and the free energy change of the reaction respectively. λ_0 is the so-called reorganization energy. The external field is regarded as a perturbation, and the electron transfer rate can be expanded as a power series in $\boldsymbol{F}$. Hereafter, the zero-, first- and second-order terms of $\boldsymbol{F}$ are considered, and other higher terms are neglected. By assuming that only ΔG is affected by $\boldsymbol{F}$, i.e. ΔG is replaced by $\Delta G_0 - \boldsymbol{\mu F}$, k_{et} in the presence of $\boldsymbol{F}$, denoted by $k_{\mathrm{et}}(\boldsymbol{F})$, is given by

$$\begin{aligned}k_{\mathrm{et}}(\boldsymbol{F}) &= A \exp[B(\Delta G_0 + \lambda_0)^2]\{1 - 2B(\Delta G_0 \\ &\quad + \lambda_0)(\boldsymbol{\mu F}) + B[1 + 2B(\Delta G_0 + \lambda_0)^2](\boldsymbol{\mu F})^2\}\end{aligned} \qquad (5)$$

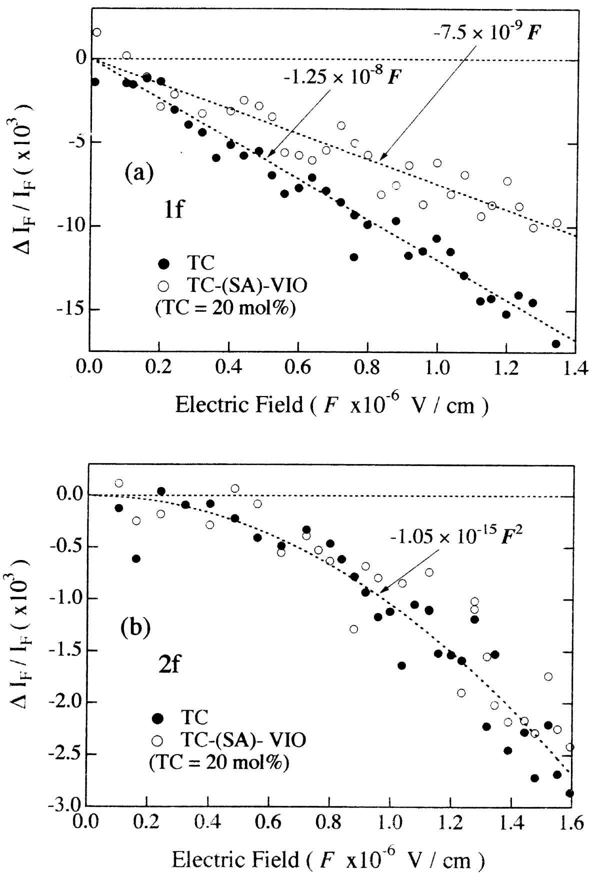

Fig. 4. Plots of $\Delta I_{\mathrm{F}}/I_{\mathrm{F}}$ for 20 mol.% of TC as a function of the applied field strength observed at 1f (top) and 2f (bottom). Filled and open circles correspond to the molecular assemblies with and without VIO respectively. The concentration of VIO was 10 mol.%. The slope of the broken line is shown in the figure.

where ΔG_0 is the free energy change in the absence of $\boldsymbol{F}$. Here, A and B are given by

$$A = \frac{2\pi}{h} \frac{J^2}{(4\pi k_{\mathrm{B}} T \lambda_0)^{1/2}} \qquad (6a)$$

$$B = -\frac{1}{4 k_{\mathrm{B}} T \lambda_0} \qquad (6b)$$

k_{et} in the absence of $\boldsymbol{F}$, $k_{\mathrm{et}}(\boldsymbol{F}=0)$, is given by $A \exp[B(\Delta G_0 + \lambda_0)^2]$. Thus Δk_{et}, which is defined as $k_{\mathrm{et}}(\boldsymbol{F}) - k_{\mathrm{et}}(\boldsymbol{F}=0)$, is given by

$$\begin{aligned}\Delta k_{\mathrm{et}} &= \{-2B(\Delta G_0 + \lambda_0)(\boldsymbol{\mu F}) \\ &\quad + B[1 + 2B(\Delta G_0 + \lambda_0)^2](\boldsymbol{\mu F})^2\} k_{\mathrm{et}}(\boldsymbol{F}=0)\end{aligned} \qquad (7)$$

In the LB films studied here, the direction of interlayer electron transfer is parallel or antiparallel to the field direction. Eq. (7) shows that the linear field effect of the decay rate depends on the direction of $\boldsymbol{F}$ and that the quadratic field effect does not depend on the field direction. The oxidation potential of TC in the ground state is 1.35 eV in solution [15], while the reduction potential of methyl viologen is -0.45 eV [16]. The wavelength of the 0–0 band of the $\mathrm{S}_0 \rightarrow \mathrm{S}_1$ transition of TC is at 435 nm. When electron transfer

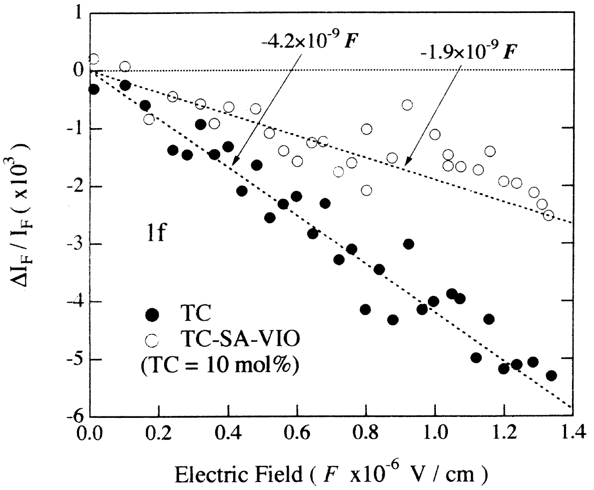

Fig. 5. Plots of $\Delta I_F/I_F$ for 10 mol.% of TC as a function of the applied field strength observed at 1f. Open and filled circles correspond to the molecular assemblies with and without VIO respectively. The concentration of VIO was 10 mol.%. The slope of the broken line is shown in the figure.

from the S_1 state of TC to VIO is considered, the value of ΔG_0 is estimated to be about 1 eV. Since the layer distance between the donor and acceptor of the present TC–VIO system, i.e. thickness of SA, is 2.5 nm, the dipole moment of the radical pair produced by electron transfer from TC to VIO is estimated to be 120 D. Thus the magnitudes of $\boldsymbol{\mu F}$ and $(\boldsymbol{\mu F})^2$ are calculated to be 0.25 eV and 6.25×10^{-2} eV^2 respectively, with a field strength of 1×10^6 V cm^{-1}. These values seem to be large enough to affect the electron transfer rate from photoexcited TC to VIO, although the precise values of ΔG_0 and λ_0 in LB films are unknown. Therefore the present field dependence of k_{et}^{VIO} and k_{et}^{SA} seems to be due to the field dependence of the free energy change for the electron transfer process. As mentioned above, the linear field effects of k_{et}^{VIO} and k_{et}^{SA} show an opposite dependence on the field direction, in the sense that one is enhanced and the other is reduced by $\boldsymbol{F}$ with a definite field direction. This result seems to indicate that the directions of the two electron transfer processes are opposite to each other. With respect to this problem, however, further study is necessary. The value of k_{et}^{VIO} at 20 mol.% of TC is larger than that at 10 mol.% of TC, as mentioned previously. The magnitude of the linear field effect of k_{et}^{VIO} at 20 mol.% of TC is larger than that at 10 mol.% of TC. These results suggest that the electron transfer rate and its field-induced change are larger for aggregates of TC, probably dimers, than for monomers. It should be noted that the electroabsorption and absorption spectra of TC show that a molecular aggregate is formed as the concentration of TC is increased in the LB films [17].

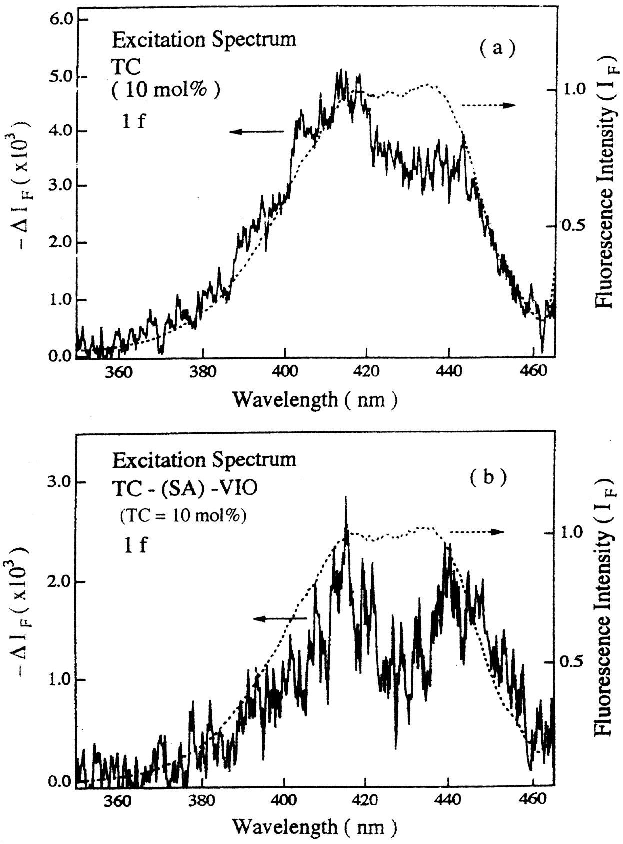

Fig. 6. Electrofluorescence excitation spectra across the $S_0\rightarrow S_1$ transition of TC for molecular assemblies without VIO (a) and with VIO (b) observed at 1f with a field strength of 1.35×10^6 V cm^{-1}, together with the fluorescence excitation spectra. The concentrations of TC and VIO were 10 mol.%. The fluorescence was monitored at 480 nm, and the maximum intensity of I_F was normalized to unity.

4. Conclusions

The fluorescence of TC, deposited as a mixed LB film, is affected by an external electric field, implying that the processes which occur between TC and the other molecules, such as the cadmium salt of SA, are affected by an electric field. In the presence of VIO, interlayer electron transfer occurs from the excited molecules of TC to VIO, and the effect of the field on the TC fluorescence is reduced. In the absence and presence of VIO, the direction of the applied field is of importance with regard to the field dependence of TC fluorescence, implying that the vectorial processes which occur between TC and the other molecules are affected by the electric field. We propose that electron transfer occurs between photoexcited TC and SA and between photoexcited TC and VIO and that both processes are affected by $\boldsymbol{F}$. The field dependences of the rate constants for the two processes were determined by combining the field dependence of the TC fluorescence intensity with the fluorescence lifetime. The linear field effects of the rate constants for the two processes show an opposite directional dependence, implying that the directions of the two vectorial processes are opposite to each other. The field dependence of the rate constant is attributed to the field-induced change in the free energy of the electron transfer processes between photoexcited TC and VIO and between photoexcited TC and SA.

Acknowledgements

We thank Dr S. Okazaki for help with the preparation of amphiphilic viologen. This work was supported by Grants-in-Aid for Scientific Research (No. 08454169) and Priority-Area-Research ‘‘Photoreaction Dynamics’’ (No. 06239202) from the Ministry of Education, Science, Sports and Culture of Japan.

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